

Comparison of the role of photon and neutron activation analyses for elemental characterization of geological, biological and environmental materials

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The potential of photon activation analysis (PAA) for multielement trace analysis can hardly compare with that of neutron activation analysis (NAA). However, PAA appears superior over NAA for the determination of a number of elements, namely C, N, O, F, Mg, Si, Ca, Ti, Ni, Sr, Y, Zr, Nb, Sn, Tl and Pb in geological, environmental and biological materials. Most of these and other elements can be determined using nondestructive, instrumental PAA (IPAA), especially in geological materials. The possibilities of IPAA for multielement analysis using photoexcitation and other photoneuclear reactions are reviewed and compared with those of instrumental NAA (INAA), namely for geological materials. The need for and usefulness of radiochemical PAA (RPAA) procedures are also discussed.

Introduction

Neutron activation analysis (NAA) employing irradiation in a nuclear reactor has gained an important position among other analytical methods for the determination of trace elements. Its main advantages, such as high selectivity and sensitivity, the virtual absence of an analytical blank, an inherent potential for accuracy and the possibility to perform simultaneous determination of a large number of elements non-destructively, using so-called instrumental NAA (INAA) have been reviewed, for instance, by BYRNE.¹ These advantages make NAA an indispensable tool for trace element analysis of various matrices. Moreover, due to its isotopic and nuclear character, determination of many elements can be performed using independent nuclear reactions and various counting modes, i.e., using the self-verification principle.²

However, as any other analytical method, NAA is not universal. For instance, determination of some low-Z elements (such as C, N, O, F) or several other elements, such as Mg, Si, Ca, Ti, Ni, Sr, Y, Zr, Nb, Sn, Tl, and Pb is interfered with, not sufficiently sensitive or impossible at all. Photon activation analysis (PAA) is a useful and complementary method to NAA, because it allows the determination of most of the above elements with a better sensitivity compared to NAA. The first review on analytical capabilities of PAA was published by LUTZ³ thirty years ago. ŘANDA et al.⁴ explored applications of instrumental PAA (IPAA) for elemental characterization of mineral materials, and a comprehensive review of the principles and applications was given by SEGBADE et al.⁵ Other authors demonstrated the usefulness of PAA for multielement analysis of different sample types, e.g., geochemical

materials,^{6,7} meteorites,^{8,9} sediments,^{10–12} sewage sludges,¹³ atmospheric particulate matter.^{14–16}

Although the potential of PAA for multielement trace element analysis (detection limits, the number of elements that can be determined) can hardly compare with that of NAA, it seems that the capabilities of PAA have not been fully exploited so far. At present, electron accelerators (LINAC, microtron, race-track microtron) as sources of bremsstrahlung for PAA provide better parameters than formerly (the mean current of electron beam of tens up to hundreds of μA). Thus, emission of bremsstrahlung up to order of 10^{14} photons per second can be obtained for the energy range of interest ($E_{\gamma} > 10 \text{ MeV}$). Subsequently, it is possible to achieve detection limits for many elements down to the $\mu\text{g}\cdot\text{g}^{-1}$ level. Increasing importance of PAA can be expected with regard to the fact that many research reactors have been shut down worldwide, and there are many countries, which have never had a nuclear reactor for NAA. In addition, electron accelerators are much more simple to operate and they produce almost no radioactive waste. The aim of this paper is to compare the analytical possibilities of PAA and NAA for various materials based on long-time experience in utilizing both methods.

Experimental

Samples and standards

Samples of biological materials were pressed to pellets of a 16 or 30 mm diameter with mass about 0.5–1 g and 2–3 g, respectively. Materials such as coal fly ash containing hard grains of silicates were pelletized using the addition of about 30% of a high purity starch.

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The pellets were placed into disk shaped polyethylene (PE) capsules and heat sealed. Geological materials (rocks, minerals, meteorites) were weighed into the PE capsules without pelletizing.

Multielement standards were prepared from weighed aliquots of elements or their compounds with well defined stoichiometry (oxides, nitrates, carbonates, etc.), which were mixed with starch and pelletized.

Irradiation

The following microtrons were employed for the studies described: (1) 30 MeV microtron of the Institute of Physical Problems, Moscow (Russia); (2) 20 MeV and 25 MeV microtrons of the Joint Institute of Nuclear Research, Flerov Laboratory of Nuclear Reactions, Dubna (Russia); (3) 20 MeV and 25 MeV microtrons of the Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague (Czech Republic), and (4) 20 MeV microtron of the Institute of Mineral Raw Materials, Kutná Hora (Czech Republic).

The microtrons were usually operated at a 10 to 20 μA electron beam current. At the 10 MeV mode (when using photoexcitation reactions) the beam current was 30 to 40 μA . Water cooled converters were made of 3 mm thick tungsten targets. Samples, standards, and monitors were irradiated in a rotation device (approximately 2 revolutions per minute) with 24 positions. The axis of rotation was perpendicular to the axis of the electron beam. The photon fluence gradient at the individual positions was within 0.3% as found using Cu monitors irradiated simultaneously with the samples and standards. More details about the experimental conditions have already been described elsewhere.^{4,17,18}

In cases where it was desirable to get a higher photon dose, the samples were irradiated in a "sandwich" arrangement in the axis of the bremsstrahlung beam. However, the photon fluence decreased quickly from 100% at the front position down to 10% at the rear position within a 10 cm distance. Up to 25 samples were irradiated in such a set. To be able to account for the decrease of the photon fluence, each position was monitored.

Counting

Gamma-ray spectrometers with various HPGe coaxial detectors with relative efficiencies of 20–50% and resolution FWHM 1.75 to 1.80 keV for the 1332 keV photons of ^{60}Co were used for nondestructive, i.e., IPAA. Three counts were usually performed after a decay for 2 to 5 hours, 1 to 2 days, and 1 to 2 weeks. For measurement of very low activities in PAA with radiochemical separation (RPAA), a well-type HP Ge detector (active volume 150 cm^3 , FWHM 2.3 keV) was

also used. Table 1 gives typical irradiation, decay, counting times employed for analysis of geological and environmental materials and the elements usually determined using the given regimes after irradiation with 20 to 23 MeV bremsstrahlung. Nuclear parameters of the radionuclides measured have been given earlier.^{3,4,19}

Results and discussion

Selection of the energy of bremsstrahlung

PAA is based on photonuclear reactions. Below the mean binding energy of a nucleon, i.e., at 8 to 10 MeV, the photoexcitation reaction (γ, γ'), also called non-elastic scattering of photon, occurs, which produces isomers for approximately 20 elements. Although the cross section of this reaction is very low, in the order of units or tens of microbarn, this IPAA mode is very selective and allows determination of several elements, such as Sr, Y, Ag, Cd, In, Ba, Hf, and Au in geological and environmental materials. For instance, an IPAA method has been developed for the determination of Au in geological materials with a detection limit of 0.1 $\mu\text{g}\cdot\text{g}^{-1}$ for 150-g samples, which is suitable for Au prospecting.²⁰ In general, this IPAA mode is not applicable for elemental analysis of biological materials, because the concentrations of the above elements are below their detection limits of this analysis mode.

Within the photon energy range of 10 to 25 MeV, the (γ, n) reaction is predominant. Its cross section at the top of the giant resonance for low-Z elements is within units to tens of millibarn and the cross section increases with increasing atomic number. It attains values of nearly one barn for the heaviest elements, which is similar to those for the neutron capture (n, γ) for many elements. Another simple photodisintegration reaction (γ, p) takes place only for low-Z nuclei (for $Z < 30$), in which the Coulomb barrier of the nucleus is relatively low. At higher energies of bremsstrahlung undesirable interference reactions ($\gamma, p+xn$), (γ, α), ($\gamma, \alpha+xn$), etc., occur.

The character of γ -ray spectra of samples irradiated with bremsstrahlung is quite different from those obtained after neutron irradiation. The annihilation line of 511 keV predominates due to the production of neutron deficient positron emitters, such as ^{11}C , ^{13}N , ^{15}O , ^{18}F , ^{30}P , $^{34\text{m}}\text{Cl}$, ^{38}K , ^{53}Fe , $^{62,64}\text{Cu}$, and others. On the contrary, the prevailing activities common in INAA, such as ^{28}Al , ^{56}Mn , ^{24}Na , ^{46}Sc , ^{140}La , ^{59}Fe , etc., which hamper the determination of other trace elements, are not produced in IPAA. From the corresponding target nuclides different products of photoactivation are formed, such as ^{26}Al , ^{54}Mn , ^{22}Na , etc., which exhibit long half-lives and, therefore, the determination of trace elements is not interfered to such a great extent as in INAA.

Unfortunately, some radionuclides (^{24}Na , $^{54,56}\text{Mn}$, ^{58}Co , etc.) are also produced by interfering reactions (n,γ), (n,p), and (n,α) caused by secondary neutrons emitted from the *W*-converter, samples itself, and construction materials surrounding the samples. Therefore, appropriate corrections must be done.

In the following sections of this paper, the authors' experience with IPAA of geological, environmental and biological samples is briefly summarized and compared with the analytical possibilities of INAA. Some applications of the radiochemical mode of PAA (RPAA) are also mentioned.

Instrumental photon activation analysis (IPAA)

Geological and environmental samples

Short-time IPAA of rocks and similar samples usually yields determination of the elements Mg, Si, K, Ca, Ti, Fe, Rb, Sr, Zr, and Ba. In combination with long-time IPAA, which allows the determination of more elements in the given sample types (Table 2), thus IPAA can almost substitute classical "shortened silicate analysis", i.e., the determination of the elements Na, Mg, Si, K, Ca, Ti, Fe, which is usually performed by wet chemistry using titration and gravimetric methods. This analysis is in demand for basic elemental characterization of geological materials. The advantage of using IPAA instead of wet chemistry assays is a lower man-power required and consequently a lower cost.

Analytical capabilities of long-term IPAA of rocks, minerals and environmental samples are compared with those offered by INAA for a variety of materials in Table 2. It follows from Table 2 that for laboratories with access to a nuclear reactor (and the possibility to perform INAA) the use of IPAA is meaningful only for the determination of those elements, which cannot be determined by INAA or only with a lower sensitivity, i.e., namely for the elements Mg, Si, Ca, Ti, Ni, Sr, Y, Zr, Nb, Sn, Tl, and Pb. On the other hand, without access to a reactor, IPAA can also successfully be used for the determination of other elements, such as Na, Cl, K, Sc, Cr, Mn, Co, Zn, As, Rb, Cs, Ba, Ce, Nd, Sm, Gd, Th, U in rock and similar samples.

There are several applications, in which the use of IPAA is superior over INAA. One of them concerns the analysis of samples with an inhomogeneous distribution of the elements of interest, such as concentrates of heavy minerals, gold ores, etc., because samples with masses up to hundreds of grams can be assayed using IPAA.

Another example is non-destructive determination of fluorine in environmental samples via the ^{18}F

radioisotope ($T_{1/2}=1.83$ h) by measurement of its non-specific 511 keV photons. Samples are irradiated with bremsstrahlung with $E_{max}=19$ MeV and counted after a decay time ranging from 2 to 5 hours. The second count is carried out after one day of decay in the same conditions and the 511 keV contribution from other positron emitters is subtracted. Analysis of the decay curve of counts registered at 511 keV can be used to check the identity of the ^{18}F radioisotope. Using this mode of analysis, fluorine concentrations ranging from 150 to 1100 $\mu\text{g}\cdot\text{g}^{-1}$ were found in a large number of lignite samples from the North-Bohemian Basin (the Most region).

A special example of the usefulness of a combination of IPAA with INAA in geochemistry can be demonstrated by our recent work aiming at elucidation of genesis of phonolites – a highly differentiated volcanic rock. For this purpose, the determination of the concentration of homologue elements, such as Sr-Ba, Zr-Hf, Nb-Ta, Y-lanthanides, and other trace elements is required. Therefore, the concentrations of Ba, Hf, Ta, and lanthanides obtained by INAA were complemented by the determination of their homologues using IPAA. Table 3 shows examples of results for geological and environmental reference materials, and for phonolites for the elements, which cannot usually be determined by INAA or for which uncertainties of INAA are larger than those obtained by IPAA. Good agreement with the literature values within uncertainty margins (if available for the latter materials) demonstrates the accuracy of our results. The only exception is the yttrium value in USGS GSP-1, which needs further elucidation.

Biological materials

Contrary to samples with a predominantly inorganic matrix, the possibilities of non-destructive determination of trace elements by IPAA in biological materials are considerably limited. With a few exceptions, the concentrations of many trace elements are mostly at the sub- $\mu\text{g}\cdot\text{g}^{-1}$ level, i.e., below the IPAA detection limit. In general, only the elements Mg, Ca, Rb, Sr, and elevated levels of Ti, As, Zr, and Pb can be determined using long-term IPAA in plant and animal tissues. More elements can be determined after preconcentration, the simplest being dry ashing. However, this leads to uncontrollable losses of volatile element species. Nevertheless, for mushrooms, which contrary to vascular plants accumulate many trace elements to a greater extent, an IPAA procedure following ashing at 500 °C yielded reliable values for the elements Mg, Ti, Mn, Ni, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Cs, Pb, Th, and U.²⁶

Table 1. Typical irradiation, decay, counting times for analysis of geological and environmental materials and the elements determined after irradiation with 20 to 23 MeV bremsstrahlung

Irradiation time	Decay time	Counting time	Elements usually determined (radionuclides measured)*
5 min	5 min	5 min	Si (^{29}Al), Cl (^{34}mCl), K (^{38}K), Fe (^{53}Fe), Zn (^{63}Zn), Rb (^{84}mRb), Sr ($^{85\text{m},87\text{mSr}}$), Zr ($^{89\text{mZr}}$), Ba ($^{137\text{mBa}}$), Nd ($^{141\text{mNd}}$)
2 to 10 h	2 to 5 h	10 to 15 min	Mg (^{24}Na), Cl (^{34}mCl), Se (^{44}Se), Ti (^{47}Ti), Fe (^{56}Mn), Zn (^{63}Zn), Sr ($^{85\text{m},87\text{mSr}}$), Nd (^{149}Nd), Ta (^{180}Ta)
	1 to 2 d	30 min	Mg (^{24}Na), Ca (^{43}K , ^{47}Ca), Sc (^{44}Sc), Ti (^{48}Sc), Ni (^{57}Ni), Zn (^{67}Cu , $^{69\text{mZn}}$), Zr (^{89}Zr), Sn (^{111}In), Cs (^{132}Cs), Ba ($^{133\text{m},135\text{mBa}}$), Nd (^{147}Nd), Sm (^{153}Sm), Gd (^{159}Gd), Pb (^{203}Pb), Th (^{231}Th)
	7 to 20 d	1 to 10 h	Na (^{22}Na), Cr (^{51}Cr), Mn (^{54}Mn), Co (^{58}Co), Ni (^{57}Co), Zn (^{65}Zn), As (^{74}As), Rb (^{84}Rb), Sr (^{85}Sr), Y (^{88}Y), Zr (^{95}Zr), Nb ($^{92\text{mNb}}$), Mo (^{99}Mo , $^{99\text{mTc}}$), Cs (^{132}Cs), Ce ($^{139,141}\text{Ce}$), Nd (^{147}Nd), Tl (^{202}Tl), U (^{237}U)

* Elevated levels of the following elements (radionuclides measured) can also be determined: Se (^{75}Se), Ag ($^{106\text{mAg}}$), Sn ($^{117\text{mSn}}$), Sb ($^{120\text{m},122}\text{Sb}$), I (^{126}I), Au (^{196}Au).

Table 2. Analytical possibilities of long-term IPAA of geological and environmental samples and their comparison with those of INAA*

Material	IPAA	INAA
Acidic rocks (granite etc.)	Na, Mg, Ca, Ti, Mn, Fe, As, Rb, Sr, Y, Zr, Nb, Cs, Ba, Ce, Nd, Sm, Th, U	Na, K, Ca, Sc, Cr, Fe, Co, (Ni), Zn, (Ga), (As), (Br), Rb, (Sr), Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Ho, Tm, Yb, Lu, Hf, Ta, (W), (Au), Th, U
Basic rocks (basalt etc.)	Na, Mg, Ca, Ti, Cr, Mn, Fe, Co, Ni, As, Sr, Y, Zr, Nb, Ce	Na, K, Ca, Sc, Ti, Cr, Fe, Co, Ni, Zn, (Ga), (As), (Rb), (Sr), Sb, Cs, (Ba), La, Ce, Nd, Sm, Eu, Gd, Tb, Ho, Tm, Yb, Lu, Hf, Ta, Th, U
Ultrabasic rocks (peridotite etc.)	Mg, Ca, Ti, Mn, Cr, Mn, Fe, Co, Ni, Zr, Nb	Ca, Sc, Cr, Fe, Co, Ni, Sb, (Sm)
Tektite	Na, Mg, Ca, Ti, Fe, Co, Ni, Rb, Sr, Y, Zr, Nb, Cs, Ba, Ce, Sm, Th	Na, K, Sc, Cr, Fe, Co, Rb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Ho, Tm, Yb, Lu, Hf, Ta, Th, U
Meteorite (chondrites)	Na, Mg, Ca, Ti, Cr, Mn, Fe, Co, Ni, Sr, Y, Zr, Y, Zr, Nb, Cs, Ce, Pb, (U)	Na, Sc, Cr, Fe, Co, Ni, Zn, As, Sb, La, Sm, Ir, Au
Coal	Na, Mg, Ca, Mn, Fe, Co, Ni, As, Rb, Sr, Y, Zr, Nb, Cs, Ce, (Th), (U)	Na, K, Sc, Cr, Fe, Co, Zn, AsBr, Sb, Cs, (Ba), La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th, U
Coal fly ash	Na, Mg, Cd, Ti, Mn, Fe, Co, Ni, As, Rb, Sr, Y, Zr, Nb, Cs, Ce, Pb, (U)	Na, K, Ca, Sc, Fe, Co, Zn, As, Rb, Sb, (Cs), La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th, U
Mn-Fe deep-sea nodules	Na, Mg, Ca, Ti, Mn, Co, Ni, Cu, As, Sr, Y, Zr, Nb, Mo, I, Ce, Sm, Tl, Pb, Th	Na, Sc, Cr, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Mo, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Ho, Tm, Yb, Lu, Hf, Ta, W, Th, U
Limestone	Mg, Ca, Mn, Ni, Sr, Zr	Na, K, Ca, Sc, Cr, Fe, Co, Zn, Ga, As, Br, Rb, Sr, Sb, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Ho, Tm, Yb, Lu, Ta, Th, U
Magnesite	Mg, Ti, Mn	Ca, Sc, Fe, Co, Br, Sb, Cs, Sm, Eu, Tb, Tm, (Ta), Th, U
Kaolin	Ca, Ti, Mn, Cr, As, Rb, Sr, Y, Zr, Nb, Cs, Ce, U	Na, Sc, Fe, Co, Ni, As, Br, Rb, Sr, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Lu, Hf, Ta, W, Th, U
Pyrite	Fe, Co, Ni, Zn, Sb, Tl, Pb	Fe, Co, Ni, Cu, Zn, As, Se, (In), Sb, Au
Sphalerite	Mn, Fe, Zn, As, Cd, In, Sn, Sb, (Tl), Pb	Fe, Cu, Zn, As, Ag, Cd, In, Sb, (Au)
Galena	Mn, Ni, Cu, Zn, As, Ag, Sn, Sb, Tl, Pb	Cu, (Zn), As, Ag, (In), (Sn), Sb
Chalkopyrite	Mn, Fe, Co, Ni, Cu, Zn, As, (Mo), Tl, Pb	Fe, Co, Cu, Zn, As, Se, Ag, Cd, In, Sb, Au
Molybdenite	Mo, Tl, Pb	Fe, Cu, Zn, As, Se, Mo, (Ag), (Sb), W, Re
Berzelianite	Mn, Co, Cu, Se, Ag, Tl	Cu, Se, Ag
Quartz	Na, Ti, Mn, Zn, Rb, Sr, Y, Zr, Nb, Ce	Na, (K), Sc, Fe, Co, (Zn), Sb, Cs, (Ba), La, Ce, Sm, Eu, Tb, (Yb), Lu, Hf, Ta, Th, U
Rutile	Ti, Cr, Zr, Nb	Cr, Fe, Sb, Hf, Ta, W
Cassiterite	Ti, Mn, Y, Zr, Nb, Sn, Ta	Sc, (In), Sn, Ta, W
Fluorite	F, Ca, Y, Ce	Ca, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, (Er), Tm, Yb, Lu, (U)
Apatite	Na, Mg, Ca, Ti, Mn, Ni, Sr, Y, Zr, Nb, Ba, Ce, Nd, Sm, Th	Ca, Cr, Sr, La, Ce, Nd, Sm, Eu, Gd, Tb, (Ho), Tm, Yb, Lu, Th, (U)
Zircon	Ti, Zr, Nb, Ce, Hf, U	Sc, Zr, (Ce), Tb, Yb, Lu, Hf, Ta, Th, U
Beryl	Na, Mn, Zn, Rb, Y, Zr, Cs	Na, Cs
River sediment	Na, Mg, Ca, Ti, Mn, Fe, Co, Ni, Zn, As, Rb, Sr, Y, Zr, Nb, Cs, Ce, (Tl), Pb, (Th), (U)	Na, K, Ca, Sc, Fe, Co, (Ni), Zn, As, Br, Rb, (Sr), Sb, Cs, (Ba), La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th, U

* Elements in brackets can usually be determined at elevated levels only.

Radiochemical photon activation analysis (RPAA)

Unlike NAA, PAA enables determination of some low-*Z* elements C, N, and O at very low concentrations, down to the $\mu\text{g}\cdot\text{g}^{-1}$ level. The products of the (γ, n) reaction – ^{11}C , ^{13}N , and ^{15}O are pure positron emitters, therefore, RPAA procedures are required for their determination. A number of papers concerning the determination of these elements has been published in the 1970's and they have been reviewed by SEGEBADE et al.³

There are also other biologically important elements, which can be determined at low levels by RPAA. One of them is fluorine, another low-*Z* element, which can be determined via the ^{18}F radioisotope (also a pure positron

emitter). Recently an RPAA procedure has been developed in our laboratory, which after a 5-hour irradiation at a 20 MeV microtron using an electron beam current of only 5 μA yielded a detection limit down to $\mu\text{g}\cdot\text{g}^{-1}$ level.²⁷ Another RPAA procedure for the simultaneous low-level determination of Pb and Tl in environmental and biological materials developed by ŘANDA et al.¹⁴ may be considered as an example of a useful, independent method, especially suitable for quality control purposes. Laboratories without access to a nuclear reactor may find useful an RPAA procedure for the determination of iodine in biological materials via the ^{126}I radioisotope described by KUČERA et al.,¹⁵ who also compared the analytical capabilities of this procedure with those provided by INAA and RNAA.

Table 3. Results of IPAA for selected geological and environmental reference materials and phonolites (in $\mu\text{g}\cdot\text{g}^{-1}$ unless otherwise stated)^{a,b,c}

Element	USGS GSP-1		USGS AGV-1		NIST 2704		BCR 277		NIST 1632a		NIST 1633B		Phonolites	
	This work	Lit. value ²¹	This work	Lit. value ²¹	This work	Lit. value ²⁵	This work	Lit. value ²⁵	This work	Lit. value ²³	This work	Lit. value ²⁴	NBPB-3	BMPH-4
Mg, %	0.583	0.579	0.93	0.922	1.20	1.20	1.17	1.00	0.11	0.12	0.509	0.482	0.41	9.95
u _c , %	± 0.012	NA	± 0.02	NA	± 0.06	± 0.024	± 0.06	N	± 0.01	± 0.02	± 0.051	± 0.010	± 0.01	± 0.20
Ca, %	1.47	1.479	3.45	3.53	2.54	2.60	5.83	6.00	0.28	0.24	1.41	1.51	0.54	4.15
u _c , %	± 0.04	NA	± 0.14	NA	± 0.13	± 0.03	± 0.82	N	± 0.06	± 0.02	± 0.12	± 0.06	± 0.08	± 0.17
Ti, %	0.40	0.39	0.68	0.629	0.40	0.457	0.307	0.300	0.143	0.165	0.65	0.791	0.126	0.80
u _c , %	± 0.02	NA	± 0.05	NA	± 0.01	± 0.018	± 0.015	N	± 0.004	± 0.010	± 0.03	± 0.016	± 0.012	± 0.03
Ni	10.7	8.8	<25	16	41	44.1	43	43.4	19	20.2	117	120.6	<11	<75
u _c	± 0.9	NA	-	NA	± 6	± 8.8	± 2	± 1.7	± 5	± 2.0	± 10	± 1.2	-	-
Sr	239	234	656	662	133	130	324	NA	81	89	984	1041	9.8	1695
u _c	± 10	NA	± 13	NA	± 2	N	± 6	NA	± 3	± 5	± 78	± 10	± 0.4	± 34
Y	86	26	20.2	20	26.8	NA	32	NA	<13	7.9	77	NA	161	54
u _c	± 5	NA	± 2.4	NA	± 4.0	± 5	± 5	NA	-	± 1.9	± 315	NA	± 9	± 5
Zr	627	530	278	227	300	300	24.0	NA	56	53	231	NA	2910	750
u _c	± 31	NA	± 28	NA	± 6	N	± 0.5	NA	± 3	± 5	± 7	NA	± 58	± 15
Nb	27.0	27.9	14.7	15	15	NA	9.7	NA	6.5	4	27.3	NA	915	160
u _c	± 1.4	NA	± 1.5	NA	± 1.5	± 1.5	± 1.5	NA	± 1.3	N	± 2.7	NA	± 18	± 3
Pb	48	55	21	36	152	161	137	146	<40	11	71	68.2	63	23
u _c	± 5	NA	± 9	NA	± 15	± 3.2	± 14	± 2.9	-	± 3	± 13	± 1.4	± 9	± 6

^a USGS GSP-1 – Granodiorite, USGS AGV-1 – Andesite, NIST 2704 – Buffalo River Sediment, NIST 1632a – Coal, NIST 1633b – Coal Fly Ash, BCR 277 – Estuarine Sediment.

^b Average of 3 to 5 replicates.

^c u_c: Combined uncertainty.

NA: Not available.

N: Noncertified value.

It follows from sensitivities of element determination by PAA, that RPAA could also be employed for assaying a whole range of other elements, such as Si, Ti, Ni, Sr, Y, Zr, Nb, Sn in various sample types at the concentration levels of $\mu\text{g}\cdot\text{g}^{-1}$ to tens of $\text{ng}\cdot\text{g}^{-1}$, provided that high-power electron accelerators, such as LINAC or microtron with electron beams with energies of 20 to 25 MeV and beam currents of tens to hundreds of μA are employed for irradiation. Some of the aforementioned elements cannot be determined at the above levels even with the aid of RNAA. However, such RPAA procedures have not been developed so far.

Conclusions

The following advantages of PAA over NAA can be pointed out:

PAA, frequently in its IPAA mode, makes it possible to determine the following elements: Na, Mg, Si, Cl, K, Ca, Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, I, Cs, Ba, Ce, Nd, Sm, Au, Tl, Pb, Th, and U in various matrices, especially in geological samples. Several of these elements cannot be determined using NAA (Table 2).

Contrary to NAA, PAA enables also the determination of several low-Z elements, such as C, N, O, F, and P at trace concentrations. Since the products of the (γ, n) reaction are pure positron emitters with non-specific annihilation radiation of 511 keV, RPAA is required for their determination.

The use of high energy bremsstrahlung in PAA eliminates the problem of neutron self-shielding in NAA for matrices with a high cross section for neutron capture, i.e., for materials with elevated levels of B, Cd, lanthanides, Au, etc.

Due to the high penetration power of high energy bremsstrahlung, large samples (with masses up to 10^2 g) can be assayed by PAA without any special facility needed in NAA. This is particularly important for samples with an inhomogeneous distribution of the elements to be determined (Au ores, heavy mineral concentrates, etc.).

Determination of several trace elements of environmental, nutritional and toxicological concern, which can hardly be achieved by RNAA, such as F, Si, Tl, and Pb, can be performed using RPAA.

A number of IPAA applications meet the demand for a fast and accurate analysis with reasonably low detection limits at an economically acceptable price.

On the other hand, PAA has also several disadvantages. In general, contrary to NAA, PAA is not suitable for analysing of submilligram samples and analytical possibilities for biological materials are considerably limited due to insufficient specificity and/or insufficiently low detection limits for a number of elements.

In conclusion, PAA should be considered as a complementary technique to NAA in well-equipped radioanalytical laboratories, because the use of both activation techniques allows the majority of elements of the periodic table to be determined. PAA is certainly an attractive radioanalytical technique for laboratories without access to a nuclear reactor. It seems that the possibilities of PAA in its RPAA mode for the determination of several important trace elements in environmental and biological samples have not been fully exploited until now. Thus, the development of such procedures may further enhance the importance of PAA as an independent analytical method needed, e.g., for quality control purposes.

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